LABORATORY INFRARED TRANSMISSION SPECTRA OF INDIVIDUAL INTERPLANETARY DUST PARTICLES FROM 2.5 TO 25 MICRONS

SCOTT A. SANDFORD AND ROBERT M. WALKER

McDonnell Center for the Space Sciences, Washington University Physics Department Received 1984 August 24; accepted 1984 November 2

ABSTRACT

Dust particles collected in the stratosphere that have chondritic elemental abundances provide a new form of extraterrestrial matter for laboratory study. Spectral transmission measurements from 2.5 to 25 μ m of 26 such particles show that almost all have a dominant 10 µm silicate absorption feature. Twenty-two of the particles can be grouped into one of three spectral classes referred to as olivines, layer-lattice silicates, and pyroxenes after the minerals that provide the best match to the dust spectra. One particle whose spectrum is dominated by anhydrous oxide minerals was also observed. Of the remaining three particles, one appears to be a mixture of olivines and pyroxenes, the second is probably a pyroxene, but the poor signal-to-noise ratio of the spectrum precludes positive identification, and the third gives no observable absorption bands. Transmission electron microscopy and laser Raman probe studies confirm the silicate mineral identifications. Complementary measurements of large D/H enrichments and solar flare nuclear tracks in some of the same particles confirm that at least some members of each spectral class are extraterrestrial. While not proven, it is likely that all particles measured are interplanetary dust particles (IDPs). The layer-lattice silicates have additional bands at 3.0, 6.0, 6.8, and 11.4 µm. The first two are probably due to water, and the second two to carbonate minerals. The published infrared spectra of protostars show features similar to those observed in the layer-lattice silicate IDPs, including the 6.8 µm feature. The possibility that this band is due to the presence of similar materials in interstellar clouds and IDPs can be tested by an astronomical search for the $11.4~\mu m$ band, which in the IDPs is correlated with the $6.8 \mu m$ feature. No single spectral dust group matches the 10 µm spectrum measured for comet Kohoutek. However, a reasonable fit can be obtained with a composite spectrum composed of pyroxenes and layer-lattice silicates (but not olivines). A test of this spectral matching would be the observation of the 6.8 µm band in comet dust spectra. Taken as a whole, the data suggest that the IDPs are composed of materials formed at an early stage of the evolution of the solar system, possibly predating the formation of the Sun. IDPs are heterogeneous and have sampled a variety of processes that will take considerable effort to decipher.

Subject headings: comets — infrared: spectra — interstellar: grains — meteors and meteorites

I. INTRODUCTION

At least one subset of dust particles collected on airborne impaction collectors flown at altitudes of 18–20 km (Brownlee 1978) is extraterrestrial in origin. Although there are several lines of evidence supporting this assertion (for earlier discussions see Flynn et al. 1978; Fraundorf, Brownlee, and Walker 1982), the most striking proofs of their extraterrestrial nature are the presence of solar noble gases (Rajan et al. 1977; Hudson et al. 1981), the presence of large deuterium enrichments (Zinner, McKeegan, and Walker 1983), and the recent discovery of solar flare tracks in mineral grains within the particles (Bradley and Brownlee 1984). Because of the interest in this distinctive form of extraterrestrial material, a cosmic dust facility has been established at the NASA/Johnson Space Center to help in the collection, curation, and distribution of samples (Clanton et al. 1982).

Particle nomenclature is somewhat confused; they have been referred to as Brownlee particles (after D. Brownlee of the University of Washington, Seattle, who pioneered their discovery and collection), micrometeorites, cosmic dust, chondritic stratospheric dust particles, and interplanetary dust particles. In this paper we adopt the terminology interplanetary dust particle (IDP) to refer to all particles whose major-element compositions relative to silicon are within a factor of 3 of those of carbonaceous chondrites (Fraundorf et al. 1982b) or that

have been proven to be extraterrestrial by the presence of solar flare tracks or large D/H enrichments.

This nomenclature implies that all stratospheric particles satisfying the chondritic composition criteria are extraterrestrial. Although this is not necessarily true, previous work has shown that this subset consists of material that is at least *mostly* extraterrestrial. The assumption that all members of the chondritic group are extraterrestrial is therefore a reasonable working hypothesis.

This hypothesis will be further tested in future work since it has now become possible to establish the extraterrestrial nature of *specific* particles. Many particles exhibit D/H enrichments (Zinner, McKeegan, and Walker 1983), and we consider the presence of a large D/H ratio as prima facie evidence that a given particle is extraterrestrial; however, the lack of such an enrichment does not preclude an extraterrestrial origin. The presence of solar flare tracks (Bradley and Brownlee 1984) can also establish that a given particle has been exposed in space, although, again, their absence does not preclude an extraterrestrial origin.

In this paper we describe infrared transmission measurements from 2.5 to 25 μ m on 26 individual dust particles that range from 10 to 40 μ m in diameter. Previous work by our laboratory first established the presence of a dominant 10 μ m absorption feature in the spectrum of a composite mount con-

sisting of three IDPs (Fraundorf et al. 1980). Higher-quality spectra of several individual particles, showing distinctive differences between individual spectra, were subsequently published (Fraundorf, Patel, and Freeman 1981). Progress in measuring and interpreting spectra has subsequently been reported in several abstracts (Sandford 1983; Sandford and Walker 1984a, b). This is the first complete compilation of data on what we hope is a statistically significant number of particles.

The initial motivation for making infrared measurements on IDPs was to test the widespread belief that the dust is derived predominantly from comets. Agreement of the IDP spectra with telescopic observations of comet dust would not prove a connection between the two, but lack of agreement could rule out a cometary origin. The comparison of laboratory data with astronomical observations remains a central theme of our work, and a separate section of this paper is devoted to a discussion of the relationship between IDPs and telescopic observations of comets and interstellar dust clouds.

It was also hoped that the infrared spectra might give useful diagnostic information about the composition of the dust particles. Early studies of IDPs showed that they are heterogeneous, with diverse mineralogical and structural properties. We shall show that the infrared spectra provide a relatively rapid, nondestructive way of initially classifying particles into different mineralogical groups.

In spite of their small sizes, it has proven possible to perform a variety of sophisticated measurements on a *single IDP* (and even on small parts of a single IDP). These include analytic electron beam techniques such as high-resolution lattice imaging and electron diffraction (Brownlee, Tomandl, and Olszewski 1977; Fraundorf 1981), ion probe isotopic measurements (McKeegan *et al.* 1984), laser Raman probe measurements (Fraundorf *et al.* 1982c), and the infrared transmission techniques discussed in this paper.

Unfortunately, at this time, only a few particles have been studied with all these techniques; we can thus give a detailed comparison of the infrared data with results obtained by other methods in only a few cases. We shall show, however, that certain patterns appear to be emerging.

Because it is possible to perform many different kinds of measurements on a single IDP, we consider it appropriate, in analogy with meteorites, to give particles individual names. We also find it easier to work with particles by name rather than by number. The names assigned to different particles have been chosen arbitrarily. One author (S. S.) is responsible for the names of most of the particles discussed in this paper. Many readers will perceive that S. S. has been influenced (perhaps appropriately) by the film "Star Wars."

II. EXPERIMENTAL PROCEDURE

The particles used in this study were originally collected on impact collectors coated with 5×10^5 centistokes silicone oil. These collectors were mounted on pylons below the wings of high-altitude aircraft and exposed at 18-20 km. We received whole collectors, either from D. Brownlee or from the Cosmic Dust Facility at JSC, after they had been exposed for 20-70 hr at altitude (typically sampling $\sim 80,000$ m³ of air). After exposure the collectors were removed and examined under a Wild M5 microscope in a laminar flow clean room.

Removal of particles from the collector was done with a thin ($\sim 5 \mu m$ diameter) glass needle mounted in a Sensaur (de Fonbrune) micromanipulator. Particles were scooped up in a

drop of silicone oil and deposited on 0.4 μ m pore size Nuclepore filter disks (13 mm diameter).

The filter disks had been previously mounted on thin quartz or metal rings and coated with carbon or palladium to provide electrical conductivity for later scanning electron microscope work. Most of the silicone oil droplet was drawn off by placing the Nuclepore filter over fritted glass connected to a water aspirator vacuum chamber. A 300 μ m diameter polyethylene micropipette was then mounted on the micromanipulator, filled with xylene, and used to immerse each grain in xylene for 1–2 minutes. This procedure removed most of the remaining silicone oil (as evidenced by subsequent measurement of the IR absorption).

For scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) analyses, the grains were simply left on the Nuclepore filter, which was attached to a standard SEM stub. A photograph and an EDX spectrum from 1 to 10 keV were taken from each particle using 20 keV electrons in a Cambridge S4-10 scanning electron microscope equipped with an Ortec Si(Li) X-ray detector with a 25 μ m Be window. The EDX data were integrated for only 200 s to minimize contamination of the particle in the SEM.

The EDX data were used to select particles of interest for further studies. Most of the particles discussed in this work were chosen because their EDX spectrum showed major heavy-element (Mg, Al, Si, S, Ca, Fe, Ni) abundances that were within a factor of 3 (normalized to Si) of those found in chondritic meteorites (see Fig. 1). Occasionally other particles were chosen for further work because they had EDX spectra similar to certain minerals found in meteorites, for example, iron sulfide grains (only Fe, S, and Ni seen in EDX) and mafic silicates (Mg, Si, and some Fe seen in EDX). Such particles are specifically noted in the results.

Once a particle was selected for additional work, it was transferred to a clean 1 mm thick quartz disk. This transfer was

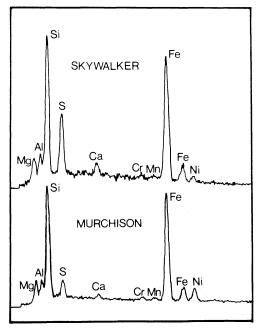


FIG. 1.—EDX spectra from a representative IDP (Skywalker) and the carbonaceous meteorite Murchison. The major elemental abundance pattern shown in these spectra is referred to here as *chondritic*.

made "dry" by picking the particle up with a sharp tungsten needle ($\sim 1~\mu m$ tip) mounted on the micromanipulator. Local charging effects on these size scales can be severe, and an alpha source was placed over the Nuclepore filter during this procedure to minimize the charging problems.

The quartz disk was then mounted in a special jig, and the particle was crushed against another quartz disk to $1-5~\mu m$ thickness. The jig is designed so that the operator can observe the crushing process through the Wild microscope and control the area on the quartz plate over which the particle fragments are dispersed. Once the crushing was finished, material from the particle would usually be found adhering to both quartz plates.

Material from one of these plates was then used to make infrared mounts, while the material on the second plate was stored for future studies with complementary analytic techniques.

The infrared mounts were made by pressing the appropriate quartz plate onto a freshly cleaved KBr crystal. The particle fragments, which stick to the KBr, were then placed over a 70 μ m aperture mounted in the infrared spectrometer. A magnetic strip was used to hold the KBr crystal in place over the aperture.

The infrared data were taken with a Nicolet 7199 Fourier transform infrared spectrometer equipped with a globar source, a KBr beam splitter, a liquid-nitrogen-cooled mercury-cadmium-telluride detector, and a $6 \times$ beam condenser. Spectra were taken at a resolution of 4 cm⁻¹ from 4000 to 400 cm^{-1} (2.5-25 μ m with $\lambda/\Delta\lambda \sim 250$ at 10 μ m).

Because of the small amount of sample material ($\sim 5-50$ nanograms) it was necessary to co-add $\sim 2\times 10^5$ interferograms over a 2 day period to obtain a reasonable signal-to-noise ratio. Experimental drifts caused by changing purge rates and thermal effects made it necessary to periodically take data through the spectrometer's front channel (no sample) for background subtraction purposes.

The spectra shown here were taken by collecting 1000 interferograms through the back beam of the spectrometer where the sample was mounted at the focus of the $6\times$ beam condenser (taking about 10 minutes), followed by the collection of 100 interferograms through the front beam. This cycle was repeated until the desired number of data had been obtained. The interferograms were then Fourier transformed, each spectrum of 1000 scans was ratioed against the corresponding spectrum of 100 background scans, and all the spectra were co-added. This entire process was then repeated with the sample moved just out of the 70 μ m mounting aperture, resulting in a spectrum of the KBr mount minus the sample. This spectrum was then used as a background and ratioed against the spectrum taken from the sample plus KBr mount, yielding the final spectrum.

Ordinarily this procedure removed all traces of absorptions by residual CO_2 and H_2O vapor in the spectrometer. However, in a few cases these features were not eliminated. The CO_2 shows up as a narrow doublet at 4.23 and 4.28 μ m, while the H_2O is seen primarily as a large number of narrow bands superposed on the spectrum from 5 to 7 μ m. These bands are probably not due to the sample and should be ignored.

An additional artifact caused by multiple reflections of the infrared source beam within the KBr mounting crystal occurs in some of the spectra. This results in a periodic oscillation being superposed on the spectrum. Again, such features are not due to the sample itself.

The tendency for the spectra to show increased transmittance with increased wavelength is *not* a thermal effect; i.e., the absorption bands are not superposed on a blackbody spectrum. The overall shape of the spectrum is dominated by wavelength-dependent scattering of the infrared beam off the sample.

In some cases, once the infrared data had been taken, the particle material was transferred to a standard transmission electron microscope (TEM) grid as follows. The particle fragments were coated with carbon, and water was used to dissolve the KBr substrate away. The particle, suspended in its carbon film, could then be manipulated onto the TEM grid.

III. EXPERIMENTAL RESULTS

Only the infrared results will be discussed in this section; relationships between the infrared data and data obtained using other analytic techniques are discussed in § IV. All but three of the particles discussed here have "chondritic" major element abundances. A brief summary of the particles (including the non-chondritic ones) is given in Table 1.

The infrared data are presented in Figures 2–5. While there is considerable variation between the spectra, it is immediately obvious that the spectra in any given figure have strong similarities, especially in the 10 μ m features. It is possible, in fact, to use the 10 μ m bands to classify the spectra into four major groups. In the following sections we show that three of these spectral groups have well-characterized terrestrial mineral analogs. The fourth group consists of those particles that do not fall into the other three classes.

As a convention we will use numbers in parentheses following band positions to list the band's full width at half-maximum in units of microns.

a) The Olivines

The spectra in Figure 2 are characterized by a distinctive 10 μ m silicate feature that consists of narrower bands at 10.1 (0.3), 11.3 (0.6), and 11.9 (0.6) μ m. The 11.9 μ m band is the strongest, followed by the 11.3 μ m band. The 10.1 μ m feature is occasionally seen as a separate, weaker band, but usually appears as a shoulder on the short-wavelength side of the overall silicate feature. An additional pair of bands can be seen between 16 and 20 μ m in all the spectra. The deeper of these two bands typically falls between 19 and 20 μ m and has a strength comparable to the 11.3 μ m band. The second band in this pair is considerably weaker and falls between 16.5 and 17.5 μ m.

It should be noted that the Sponge 1 and Sponge 2 spectra were taken from different halves of the same IDP. This particle was found in close proximity to the particle Essex, and the two particles may be fragments of a single larger particle that broke up on impact with the collector.

All the spectra match well with data from terrestrial olivines (see the bottom spectrum in Fig. 2), and for this reason we refer to these particles as *olivines*. The bands near 10 μ m are associated with Si–O stretching vibrations, and the longer-wavelength bands are attributed to Si–O–Si bending vibrations (Farmer 1974a). The slightly larger width of the 10 μ m band in the terrestrial olivine is caused by matrix effects (the standard samples were all ground in KBr and pressed into 100 mg pellets).

The exact positions of all the bands in olivine spectra are a function of the radius of the constituent cations (Tarte 1965), with the bands near 10 μ m varying over a 0.5 μ m range and

INFRARED SPECTRA OF IDPs

TABLE 1
SUMMARY OF THE INTERPLANETARY DUST PARTICLES EXAMINED IN THIS STUDY

:		Dimensionsa			
Name	Number	(μm)	EDX Spectrum	IR Class	Appearance in the SEM
Toad	u21-M9-7	19 × 11	"chondritic"	olivine	Elongated compact aggregate of 1–5 μ m grains
Marvel	u13-M10-4	15×15	"chondritic"	olivine	Compact aggregate of 0.5-2 µm grains
Sponge 1	r21-M4-3B	32×30	"chondritic"	olivine	Reentrant aggregate of 1-2 μm grains
Sponge 2					
Essex	r21-M4-3A	35×20	"chondritic"	olivine	Reentrant aggregate of 1–2 μ m grains
Jedai	r21-M2-3	21×21	"chondritic"	olivine	Compact aggregate of 1-5 μ m grains
Attila	r21-M2-8	30×18	"chondritic"	olivine	Elongated grain, adhering submicron grains
			plus K, P, and Zn		
3U2's	u18-M4-1A	15×10	"chondritic"		Reentrant aggregate of 1-5 μ m grains
	u18-M4-14B	10 × 6	"chondritic"	pyroxene	Highly reentrant aggregate of 0.1–0.5 μ m grains
	u18-M4-9C	12 × 12	"chondritic"	pyronene	Not imaged in SEM
Spray One	u23-M4-4A	23×20	"chondritic"	pyroxene	Highly reentrant aggregate of 0.5-1 μ m grains
Spray Two	u23-M4-4B	19×18	"chondritic"	pyroxene	Highly reentrant aggregate of 0.5–1 μ m grains
Key	u23-M3-7	33×13	"chondritic"	pyroxene	Elongated compact single grain
Mac	u23-M10-5	25×10	"chondritic"	pyroxene	Compact aggregate of 1-2 μ m grains
Dumpy	r18-M2-6	19×10	Mg and Si	pyroxene	Single smooth compact grain
			with minor S,	• •	
			Ca, Cr, Mn, and Ni		
Low-Cal	u21-M2-1	25 × 16	"chondritic"	LLSb	Compact aggregate of 1–5 μm grains
Big Guy	r18-M4-8	41×40	"chondritic"	LLS^b	Single grain
Molar	r21-M4-6	24×19	"chondritic"	LLS^b	Single smooth grain
Xavier	r21-M4-1	19×13	"chondritic"	LLSb	Single smooth grain
Skywalker	r21-M3-5A	35×25	"chondritic"	LLSb	Reentrant aggregate of 1-5 μ m grains
Lea	r21-M2-4	17×11	"chondritic"	LLSb	Single smooth grain
Banana	u23-M1-3	46×17	"chondritic"	LLS^b	Elongated aggregate of 1-5 μm grains
Calrissian	r21-M1-9A	33×25	"chondritic"	LLS ^b	Compact aggregate of 1-5 μ m grains
Yoda	r21-M3-6	33×19	"chondritic"	LLSb	Reentrant aggregate of 1-5 μ m grains
Speckles	u21-M4-8	22×16	"chondritic"	LLSb	Single smooth grain
Manny	u13-M6-1A	15×15	"chondritic"	LLS^{b}	Single smooth grain
Folsum	r18-M4-9	12×8	Mg and Si	other	Single smooth grain with an adhering clump
			with minor S,	_	of highly reentrant 0.5–2 μ m grains
			Cr, Mn, and Ni		5,
Big Bang	u21-M2-3	14×14	"chondritic"	other	Reentrant aggregate of 0.5–2 μ m grains
Whirlpool	u21-M2-5	14×14	"chondritic"	other	Highly reentrant aggregate of 0.5–2 μ m grains
Conehead	u13-M4-2A	25×20	"chondritic"	other	Single smooth grain

^a Length and width as measured off an SEM photo.

the 16–20 μ m features varying up to 1.5 μ m in position. All the IDPs in Figure 2 show spectra consistent with olivines falling within the forsterite (Mg₂SiO₄)–fayalite (Fe₂SiO₄) solution series.

The small, narrow band seen at 7.9 μ m in some of the spectra (Sponge 1, Essex, and Jedai) will be discussed in the next section.

b) The Layer-Lattice Silicates

The IDP data in Figures 3 and 4 all share similar spectral features, although there is substantial variation within the group. Spectra showing the largest variations from the "norm" in this class have been placed in Figure 4.

The spectra in these figures are characterized by a relatively narrow, roughly symmetrical absorption band centered near $9.8 (2.0) \mu m$ which is featureless, unlike that in the olivines.

Most of the spectra in this group have additional bands at 3.0 (0.3), 3.4 (<0.1), 6.0 (0.5), 6.8 (0.7), 7.9 (0.1), and 12.5 (0.6) μ m. Some of the spectra (Low-Cal, Skywalker, and Calrissian) also have a band or shoulder near 11.4 (0.4) μ m. All the spectra have one or two additional bands between 14 and 23 μ m that are of comparable strength to the 9.8 μ m band and have FWHM between 3 and 7 μ m. The 6.8 and 11.4 μ m band depths appear to be correlated, as do the 7.9, 12.5, and possibly

a component of the 3.4 μ m band depths. However, the relative depths of these groups of bands do not correlate with each other or with any of the other bands.

The 9.8 μ m band in these spectra is characteristic of minerals containing layer-lattice structures (Farmer 1974b), and for this reason we refer to particles falling into this group as *layer-lattice silicates*. The 9.8 μ m band is associated with Si–O stretching vibrations, and the 14–23 μ m bands are associated with Si–O–Si bending vibrations. For comparison, the second spectrum from the bottom in both Figures 3 and 4 is of chlorite, a terrestrial layer-lattice silicate. The bottom spectrum in both figures is of the carbonaceous meteorite Murchison, which is known to contain abundant layer-lattice silicates.

The IDP bands centered at 3.0 and 6.0 μ m are seen in many terrestrial layer-lattice silicates and are attributed to water of hydration in the mineral (Farmer 1974b). The 3.0 μ m band is caused by O–H stretching vibrations, and the 6.0 μ m band by H–O–H bending vibrations. The depths of these bands relative to the 10 μ m silicate band are variable and may reflect water loss caused by heating experienced when the particles entered the Earth's atmosphere (Fraundorf 1980). The variability could also be due to differing amounts of original water or to differential adsorption of terrestrial water since arriving at Earth.

The 3.4, 7.9, and 12.5 μ m bands are probably associated with

^b Layer-lattice silicate.

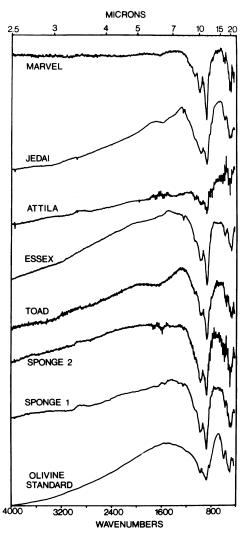


Fig. 2.—Data from the six IDPs that fall into the olivine spectral class. The bottom spectrum is from a terrestrial olivine.

a component containing C-H bonds. Unfortunately, the silicone oil medium used to collect the particles also exhibits features at these locations, and the possibility exists that these bands are the result of silicone oil contamination. Layer-lattice silicates are known for their affinity for absorbing liquids, and this would explain why similar bands are not usually seen in the spectra from the other groups.

The 3.4 μ m band is, however, substantially wider in many of the spectra (Big Guy, Molar, Xavier, and Lea) than the band observed for pure silicone oil (the 3.4 μ m feature in Skywalker is as wide as that normally seen in silicone oil), and in these cases it may contain some contributions from original hydrocarbons contained within the particles. Deuterium enrichments that exist in some of the particles are known to correlate with carbon abundance (Zinner and McKeegan 1984), implying that these particles do, in fact, contain indigenous hydrocarbons. Thus, the 3.4 μ m band may consist of two independent components, silicone oil contamination and primitive hydrocarbons. Because of the uncertainty caused by the possibility of contamination, these bands will not be discussed in further detail.

We believe that the 6.8 μ m band is probably due to asym-

metric stretching vibrations of carbonates. This band is seen in most of the particles in this group and is considerably stronger than the similar, faint band seen in the Murchison spectrum.

The carbonate identification is strongest for the particle Calrissian (see Fig. 4), which has a 6.8 μ m feature that is deeper than its associated silicate band. This particle has an additional narrower and weaker 11.4 µm band characteristic of CO₃ scissors vibrations. The position of this band varies between 11.2 and 11.5 μ m depending on the cation associated with the CO₃ (White 1974) and is consistent in this case with a Ca-Fe carbonate. However, while Calrissian has a higher than average Ca abundance, the Ca and Fe concentrations in the layerlattice silicate particles do not, in general, correlate with the depths of the 6.8 μ m bands. The 6.8 μ m band shape is most consistent with the calcite structure of carbonates and not the aragonite structure. Preliminary Raman measurements (B. Wopenka, private communication) and electron diffraction data (P. Fraundorf, private communication) on Calrissian are also consistent with the carbonate identification, but more work will be required to make this identification certain.

Several of the spectra in the layer-lattice silicate group exhibit unique features, and these have been placed in Figure 4.

Big Guy has all the bands usually associated with particles in this group but has an additional narrow band at 7.3 (0.1) μ m superposed on the shoulder of the 6.8 μ m carbonate feature. The source of this band has not yet been identified.

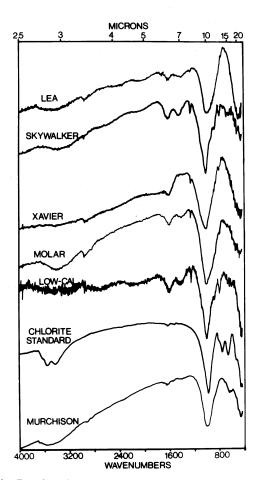


Fig. 3.—Data from five IDPs in the layer-lattice silicate spectral class. The second spectrum from the bottom is from a terrestrial chlorite (a layer-lattice silicate). The bottom spectrum is from the carbonaceous meteorite Murchison.

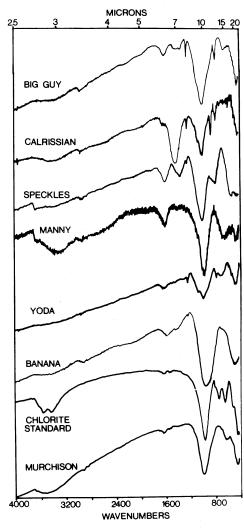


Fig. 4.—Data from six IDPs in the layer-lattice silicate spectral class. The second spectrum from the bottom is from a terrestrial chlorite (a layer-lattice silicate). The bottom spectrum is from the carbonaceous meteorite Murchison.

Speckles has broad unidentified bands at 7.3 (0.7) and 12.4 (1.8) μ m. These bands are *not* consistent with the 6.8 and 11.4 μ m bands seen in the other layer-lattice silicate IDPs, and the source of these bands has not yet been identified.

Both Speckles and Manny show evidence of a narrow absorption at $2.7~(<0.1)~\mu m$ superposed on the broad $3.0~\mu m$ hydration feature. Similar bands are seen in some layer-lattice silicates and are attributed to the stretching vibrations of structural OH in the mineral (Farmer 1974b). Manny is also unique among the layer-lattice silicate particles in having almost no $6.8~\mu m$ carbonate band.

Yoda shows a band at 9.2 (0.1) μ m that is not seen in the other particles. While the identification of this band is not certain, it may be due to atmospheric heating. Heating studies of analog Murchison material have shown that at temperatures of ~800°C the 3.0 μ m band in the spectra disappears, the 6.0 μ m band is greatly reduced in strength, and the 10 μ m silicate band begins to alter. At even higher temperatures the silicate band changes to that of pyroxenes and olivines. However, this band could also be caused by sulfates, which have features in this spectral region.

Banana has a 10 μ m silicate band with a FWHM of $\sim 3 \mu$ m, which is broader than that seen in the other layer-lattice silicate particles. This is probably an artifact. We had difficulty crushing this particle as flat as the other particles, and the apparent width of the silicate band is probably due to optical saturation effects.

c) The Pyroxenes

The IDP spectra falling in the third spectral group for which we have identified a mineral analog are shown in Figure 5. The silicate features in these spectra are highly variable (no two are identical), and these particles have been placed in the same group primarily because their overall $10~\mu m$ bands have similar positions and widths.

The first spectrum in Figure 5, 3U2, has bands of roughly equal strength at 8.8 (0.4), 9.4 (0.3), 9.9 (0.1), 10.8 (0.3), 11.9 (0.5), 14.0 (1.8), and 16.7 (1.1) μ m and a stronger band near 20.0 (1.7) μ m. Weaker bands are seen at 6.3 (0.4), 7.3 (0.3), and 8.0 (0.2) μ m. Particle Spray One has bands at similar positions but differs from 3U2 by having weaker bands at 8.8 (it only shows up as a shoulder), 11.9, 20.0, and 23.5 μ m. Spray One and Spray Two were taken from a group of particles found together on an impact collector, and these IDPs may be related. The Spray Two spectrum is similar to that of Spray One, although the data are not as good. The major difference between Spray One and Spray Two is that the latter does not show the

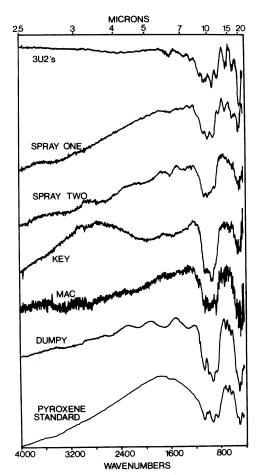


Fig. 5.—Data from five IDPs in the pyroxene spectral class. The bottom spectrum is from a terrestrial pyroxene.

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detailed bands above 11.1 μ m present in the former. Instead, Spray Two has only a single band centered at 19.2 μ m with a FWHM of about 7 μ m. Key also has a single band at 20 (2.7) μ m, but its 10 μ m silicate band shows two distinct features, a band at 10.5 (0.6) μ m and a strong wide shoulder centered at 9.6 (1.0) μ m. The spectrum of Mac has poor signal-to-noise ratio but clearly shows the silicate band at 10 (2.9) μ m and another band at 21.1 (6.6) μ m. There is some hint of detailed features within the silicate band at 9.4, 10.2, and 11.3 μ m. Dumpy shows strong bands at 9.3 (0.4), 9.9 (0.1), 10.8 (0.5), 11.4 (0.3), and 19.7 (3.6) μ m with weaker bands at 13.7 (0.3), 14.7 (0.2), and 15.5 (0.3) μ m.

While all these spectra differ, they all show similarities with spectra of terrestrial pyroxenes (see bottom spectrum in Fig. 5), and we refer to IDPs in this group as pyroxenes. The mineral pyroxene has an $X_2Y_2O_6$ structure, where Y is usually Si and X can be any one of a wide variety of cations. Because of this mineral's range in possible compositions, it is not surprising that terrestrial pyroxenes show a great deal of spectral variability (Liese 1975). If all the IDPs in Figure 5 are really pyroxenes, then the variations in band positions, strengths, and numbers are probably due to different chemical compositions.

Because of this variability, it is generally difficult to identify the IDP spectra with a particular pyroxene. However, for 3U2 the spectrum is found to match well with that of the pyroxene enstatite $(Mg_2Si_2O_6)$.

d) Other Particles

Four of the particles examined had infrared spectra that did not fall into any of the previously discussed groups. Their spectra are shown in Figure 6.

Folsum has a 10 μ m silicate band that contains features at 9.3 (0.4), 10.7 (0.5), 11.1 (0.2), and 11.6 (0.3) μ m. Additional

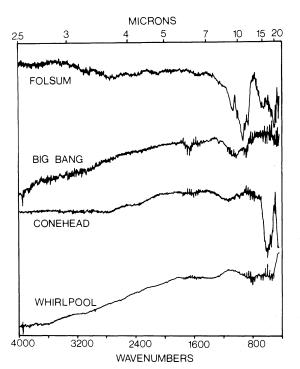


FIG. 6.—Data from the remaining four IDPs measured. Folsum may contain a pyroxene-olivine mixture, and Big Bang may contain pyroxenes. Conehead probably consists of anhydrous oxide minerals. Whirlpool appears to contain no major infrared-active components.

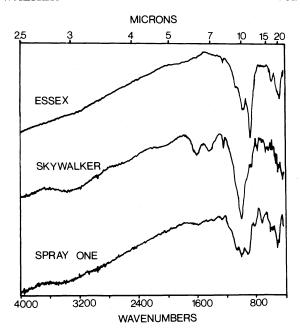


Fig. 7.—A comparison of the three major infrared spectral IDP classes. From top to bottom are representative spectra of the olivines (Essex), the layer-lattice silicates (Skywalker), and the pyroxenes (Spray One).

bands are seen at 15.4 (1.4) and 19.3 (2.3) μ m. This spectrum matches reasonably well with that found from mixtures of terrestrial olivines and pyroxenes. This particle was seen in the SEM to consist of two components, a single grain and adhering "fluffy" material, and thus, it may contain material from both the olivine and pyroxene IDP groups.

Big Bang has a weak 10 μ m silicate band and a weak 6.0 μ m feature. The silicate band shows evidence of features at 9.7 (1.1) and 11.2 (0.5) μ m. The width and position of the silicate band is comparable to that seen in pyroxenes, but because of the poor quality of the spectrum and the uncertainty of the identification, we have chosen to include this particle in the "other" group. The 6.0 μ m band is probably due to water.

Conehead shows strong absorptions at 16.8 (3.9) and 23.1 (3.4) μ m. Absorptions in this region, when not attended by a 10 μ m silicate band, are characteristic of anhydrous oxide minerals (Farmer 1974c). We find the best matches to this spectrum with minerals of the structural form X_2O_3 , where X is Al or Fe.

Whirlpool fails to show any major absorption bands and must therefore consist primarily of phases that are infrared inactive.

e) Absorption Coefficients

Figure 7 contains a representative spectrum of each of the three major spectral groups seen in the IDPs.

The absorption coefficients for the IDPs are difficult to determine. Large errors are introduced by variations in the spectrometer's source intensity and transmission efficiency over the 2 day measuring period, the lack of precise thickness measurements on the samples, and uncertainties in the fraction of the beam intercepted by the particles. Because of these difficulties, we can only say that the three IDP spectral types have roughly comparable absorption efficiencies, and that they appear to be approximately consistent with those of the appropriate terrestrial analog minerals.

IV. DISCUSSION

In the previous section we showed that most IDPs fall into three spectral classes given names suggested by similarities with terrestrial mineral standards. Here we treat the following questions: (a) To what extent are the infrared classes related to the morphologies and mineralogies of the particles as measured by scanning electron microscopy and (b) transmission electron microscopy? (c) How are the infrared classes related to isotopic measurements? (d) How do the spectra of the IDPs compare with astronomical data on comets and interstellar dust clouds? (e) What additional work needs to be done to clarify the relationship between IDPs and astronomical objects? (f) What does the ensemble of results imply about the origin of IDPs?

Only a few of the particles for which infrared data exist have been studied with other techniques. Thus the answers to the above questions are incomplete. In spite of this, certain patterns appear to be emerging, and tentative conclusions can be made.

a) Comparison of the Infrared Classes with SEM Observations

SEM photographs can be used as an initial method of classifying IDPs into different groups. At one extreme of a morphological classification are particles that have been variously described as "fluffy," "fine-grained reentrant," "porous," and "fragile." They typically consist of loose aggregates of ~ 0.1 μ m building blocks stuck together in what has been called a cluster-of-grapes structure (a typical picture of such a particle is shown in Fig. 6 of Fraundorf, Brownlee, and Walker 1982). The other end of the morphological spectrum is represented by smooth spherules that look like they solidified from a single liquid drop. Almost all particles in this latter category consist of aluminum oxide debris from rocket exhaust (Brownlee, Ferry, and Tomandl 1976), and none of the particles described in this paper fall in this category. The morphologies of most of the particles that we have studied lie between these two extremes and are difficult to classify quantitatively. The last column of Table 1 represents our best attempt to convey in words the appearance of particles in the SEM. For representative photographs of particles described as either "compact" or "smooth" the reader is referred to Figures 4 and 5 of Fraundorf, Brownlee, and Walker (1982).

Because porous particles are inherently more photogenic, they probably tend to be overrepresented in the published pictures of IDPs. The particles studied here come predominantly from a few collectors, and a conscious effort was made to select particles only on the basis of size and composition and not by any other criterion. As can be seen from Table 1, most of the particles were *not* of the fluffy, porous type but instead were more frequently described as smooth or compact.

Not enough systematic work has been done on different collectors to determine whether the proportion of particles in different morphological classes varies between collectors flown at different times. It is our qualitative impression that the relative proportions are probably fairly constant if no picking bias is introduced. Unfortunately, we (and probably others) tended to preferentially select the more porous particles when we first started work on interplanetary dust. This selection effect probably stemmed partly from the fact that most porous particles have chondritic compositions, and partly from the fact that we were aware that studies of the deceleration of meteors in the atmosphere had shown that many of them must be rather low density particles (Verniani 1973).

The results shown in Table 1 appear to indicate that the

pyroxene infrared class is composed primarily of porous particles, while the layer-lattice silicate class is composed predominantly of smooth, compact particles. However, examples of both porous and smooth particles are found in all infrared categories, and there is not yet enough data to warrant a final conclusion on this point.

b) Comparison of the Infrared Classes with TEM Observations

Two particles in the layer-lattice silicate class, Low-Cal and Skywalker, have been studied by the Arizona State group using high-resolution transmission electron microscopy (Tomeoka and Buseck 1984a, b). Low-Cal shows an abundance of layer-lattice silicates with interlayer spacings of 10–12 Å which have been interpreted as being caused by smectites or mica. The lattice spacings, as well as the poor state of order of the individual crystals, distinguish the layer-lattice silicates in Low-Cal from those in carbonaceous meteorite matrices. The latter have ~7 Å interlayer spacings that correspond to septachlorite or serpentine minerals. The observation of low-Ni pentlandite (Fe, Ni, S) crystals in Low-Cal is unique to the IDPs. Some forsteritic olivine crystals (Mg₂SiO₄) are seen in Low-Cal, while in contrast, olivines in carbonaceous chondrites show a wide range of Mg/Fe ratios.

Skywalker differs considerably from Low-Cal and appears to be more closely related to carbonaceous meteorites. Two types of abundant layer-lattice silicates have been confirmed in this particle by the TEM observations. The first type is similar to that seen in Low-Cal, while the second is more Fe-rich and Mg-poor. In contrast to Low-Cal, where olivine crystals are rare and pyroxenes are not observed, Skywalker has an abundance of pyroxenes, including the mineral fassaite [Ca(Mg, Al, Ti)(Si, Al)₂O₆], which is a common constituent of Ca-rich and Al-rich refractory inclusions (CAI) in carbonaceous meteorites such as Allende (Grossman 1980). Many CAIs have been shown to contain isotopic anomalies in a number of elements (Begemann 1980).

The IDPs Low-Cal and Skywalker, and matrix samples of the carbonaceous meteorite Murchison, all have similar layer-lattice silicate infrared spectra. TEM observations show abundant layer-lattice silicates in all three, confirming the choice of the infrared nomenclature. At the same time, the TEM observations show significant differences between the three objects, and it is clear that the layer-lattice infrared class is composed of particles with different microstructures.

Two particles in the infrared olivine class, Jedai and Attila, have been examined by high-resolution electron microscopy at Arizona State University (R. Christoffersen, private communication). In Jedai, eight single crystals larger than 500 Å in size were measured both by electron diffraction and by EDX techniques. All the crystals were olivine of forsteritic (Mg₂SiO₄) composition. No layer-lattice silicates were observed. Attila also contains abundant olivines. The infrared classification of the olivine particles is thus confirmed.

Attila is important for several other reasons as well. Christoffersen has found it to contain a form of Zn–Fe sulfide not previously seen in any of the IDPs. In addition, he finds abundant solar flare tracks in the olivine crystals of Attila, thus demonstrating that at least some of the particles in the infrared olivine class are definitely extraterrestrial.

Spray One, the one pyroxene infrared type studied by TEM, has received only a cursory examination (J. Bradley and R. Christoffersen, private communications). The particle is complicated, consisting of myriad small crystallites embedded in a matrix of low-Z composition. Both pyroxene and olivine crys-

tals appear to be present, but the relative proportions are unknown. No layer-lattice silicates are seen. The small sizes of the crystals make single-crystal electron diffraction work difficult, and further study will probably require application of the polycrystal electron diffraction analysis technique developed by Fraundorf (1981) in earlier TEM work on a set of nine other IDPs.

A composite mount consisting of three individual IDPs and named 3U2 also has an infrared spectrum that is dominated by pyroxene, although some admixture of olivine may be present. A relatively large Mg-rich pyroxene crystal was identified in this mount using laser Raman microscopy (Fraundorf *et al.* 1982c). The choice of infrared nomenclature for the pyroxene class thus also appears to be confirmed, although additional mineralogical work is needed.

Overall, it appears that the infrared classification gives a useful indicator of the *major* silicate phase present in the particles

In contrast to TEM observations, which are laborious, the infrared spectrum of a particle can be obtained relatively rapidly (2 days). The infrared spectrum also gives a global "whole rock" view of a particle that is difficult to achieve when using high-magnification TEM methods. Moreover, the infrared spectrum, as in the case of Calrissian, can be used to identify phases such as carbonates that have yet to be identified in the TEM. The infrared has the added advantage of being able to monitor the 3.0 μ m and 6.0 μ m bands, which are indicators of water within the particles. Water is a potentially important constituent since it represents one of the reservoirs of hydrogen in the particles.

The infrared spectra are also useful in locating unusual particles, such as Conehead, that do *not* fall into the standard categories. This could be particularly important in searching for particles that consist primarily of refractory oxides that could have formed as primary condensates from a hot gas.

However, since IDPs within a given infrared class can differ substantially when studied in the TEM, it is clear that an infrared spectrum alone cannot give a complete description of a particle. This is illustrated by the fact that a spectral analog can be found among the various meteorite types for each of the three major IDP spectral classes (Sandford 1984) although the two types of extraterrestrial materials have different microscopic structures and were undoubtedly formed by different processes.

Infrared spectroscopy has the disadvantage that it is insensitive to the detection of certain components known to be in the IDPs. To be infrared-active, a molecular vibration must involve a change in dipole moment, so components like graphite and pure metals have no characteristic absorption features in the mid-infrared. Many minerals which are abundant in IDPs (Fraundorf 1981), such as magnetite (Fe₃O₄), have their major absorption features at wavelengths greater than 15 μ m. Band identifications in this region can be confused by the Si–O–Si bending mode features and lattice mode features from many other minerals. For these reasons the 2.5–25 μ m infrared spectra do not allow identification of all the phases present in a particle. Future work at longer wavelengths may partially alleviate this problem.

c) Comparison of the Infrared Classes with Isotopic Measurements

In this section we discuss the isotopic data obtained from IDPs. Such studies offer one of the strongest means at our disposal to verify the extraterrestrial nature of individual IDPs.

Three IDPs classified as layer-lattice silicates, Skywalker, Calrissian, and Lea, have been examined in the Washington University CAMECA IMS-3F ion probe (McKeegan *et al.* 1984; McKeegan, Walker, and Zinner 1985). The first two show variable D/H enrichments in different fragments, with Skywalker showing a maximum value of $\delta D = +767\%$ (parts per thousand) and Calrissian a maximum value of $\delta D = +1913\%$, where δD is defined as

$$\delta D \equiv \left[\frac{(D/H) \text{ sample}}{(D/H) \text{ standard}} - 1 \right] \times 1000 ,$$

the standard D/H ratio being obtained from terrestrial actinolite.

These high values demonstrate that these particles are both extraterrestrial and consist of primitive solar system material (Zinner, McKeegan, and Walker 1983). The deuterium anomaly in Skywalker has been shown to be correlated with a carbonaceous component and *not* with the water that is evident in the infrared spectrum (Zinner and McKeegan 1984). The Calrissian result is particularly significant because of the importance of this particle in the identification of the 6.8 μ m feature as a carbonate band.

Lea, in contrast, shows δD -values ranging from -280% to +199%. This range is outside the precision of the measurements and shows that Lea, like the other two layer-lattice IDPs, is heterogeneous. The relatively large depletion observed in one fragment, and the moderate enrichment in another, suggest that Lea is also extraterrestrial, although the case is not as clear-cut as for Skywalker and Calrissian.

Only one particle in the pyroxene infrared class, Spray Two, has been studied with the ion probe. Spray Two has a $(\delta D)_{max} = 993\%$ and must also be extraterrestrial.

Two particles in the olivine infrared class, Essex and Attila, have been measured in the ion probe. Essex exhibits moderate D depletions ranging from $\delta D = -193\%$ to -120% and is possibly extraterrestrial. Attila has δD -values from -21% to +73%. These values span those observed in terrestrial samples and give no evidence of an extraterrestrial origin. Attila, however, is known to be extraterrestrial because it contains abundant solar flare tracks.

Thus, individual particles from the olivine, layer-lattice silicate, and pyroxene classes have been shown to be extraterrestrial. Whether all particles in these infrared classes are extraterrestrial is impossible to say at this time. Additional isotopic and track studies should clarify this question.

d) Comparison of the Spectroscopic Properties of IDPs with Astronomical Observations of Comets and Interstellar Dust Clouds

One of the principal motivations for measuring the IR properties of IDPs was to test the widespread belief that most interplanetary dust is derived from comets. If this is true, then we would expect the IDP spectra to match well with cometary spectra. A perfect spectral match would not *prove* a cometary origin for the dust, but a mismatch could *disprove* the connection.

Interplanetary dust must come from a variety of sources, but several arguments suggest that comets provide the majority of the dust mass. Meteor showers are known to be associated with specific comets (Hughes 1978; Wetherill and ReVelle 1982). Sporadic meteors may be derived from shower streams and thus may also have a cometary origin (Dohnanyi 1982). The dust grains responsible for meteors are, of course, much

larger than the particles studied here. However, it is reasonable to believe that IDPs are simply smaller versions of the particles that give rise to visual meteors. For example, optical measurements and rocket-borne mass spectrometers have demonstrated that meteor shower particles have chondritic compositions (Herrmann et al. 1978; Millman, Cook, and Hemenway 1973; Harvey 1973). Further, considerations of the deceleration of meteors show that many of them must have low mass-to-surface ratios (Verniani 1973). Direct density measurements show that some IDPs have densities less than 1 g cm⁻³ (Fraundorf et al. 1982a), and the presence of "splatters" of material on the collectors (Fraundorf et al. 1982b; Brownlee, Tomandl, and Olszewski 1977) shows that many particles are very fragile assemblages, suggesting that many have even lower average densities.

Another argument for a cometary origin is based on mass-balance. Studies of micro-impact craters on lunar rocks show that the flux of micrometeorites has not changed appreciably in the last 10^6 yr (Morrison and Zinner 1975). Further, studies of impact craters and solar flare tracks on crystals removed from depth in lunar cores indicate that the flux of micrometeorites has been relatively constant for the last 10^9 yr (Poupeau *et al.* 1977). Since the calculated Poynting-Robertson lifetime for $10 \mu m$ particles at 1 AU is $\sim 10^4$ yr (Dohnanyi 1982), a constant source that replenishes the interplanetary dust cloud must exist. Calculations indicate that comets could provide such a source (Whipple 1982), although the arguments are not compelling.

The IDPs could be derived from the same sources as larger extraterrestrial objects that arrive at Earth, namely, the meteorites. However, meteorites and IDPs differ in many respects (Fraundorf and Shirck 1979). Meteorites are widely believed to be derived from asteroids, and, if this were true, and a separate source for IDPs were required, then comets are the logical alternative. We should point out, however, that studies of cosmic spherules found in sea sediments indicate that many meteorite-sized objects of possible asteroidal origin that arrive at Earth may be too fragile to survive entry and reach the ground (Brownlee et al. 1980).

In Figure 8 we show characteristic absorption spectra in the 10 μ m region for the major IDP classes compared with (inverted) emission spectra of the dust tail of comet Kohoutek (Merrill 1974). The spectral properties of the comet dust were derived by subtracting an average blackbody spectrum from the raw data. It clearly would be desirable to compare the emission spectra of IDPs with the comet data, but this is currently beyond our technical capabilities. Absorption and emission spectra of standard minerals show similar spectral features (Rose 1979), and the 10 µm silicate bands seen in absorption and emission in astronomical observations have similar structure (compare, for example, Fig. 1 in Willner 1977 with Fig. 2 in Merrill and Stein 1976), so to first order a direct comparison of the data seems reasonable. Because of differences in the manner in which the astronomical and the laboratory data were taken, we do not attach importance to the overall shape of the spectra over long wavelength intervals. However, we do consider the positions of specific spectral features and the overall width of individual bands to be significant. Nonetheless, it should be kept in mind that the necessity of comparing absorption and emission data is a fundamental limitation of the present work.

It can be seen that no one of the IDP spectral types fits the comet data. This is hardly surprising since each of the IDP

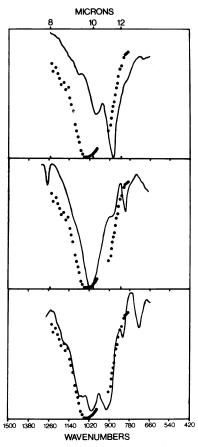


FIG. 8.—Comparisons of the three IDP spectral classes with inverted comet Kohoutek emission data. From top to bottom are comparisons with an olivine (Essex), a layer-lattice silicate (Skywalker), and a pyroxene (Spray One). The solid points are the cometary data.

spectral classes corresponds to specific mineral types, while the broad and featureless 10 μ m comet feature has previously been attributed to "amorphous silicates" (Hanner 1980; Krätschmer and Huffman 1979).

It is conceivable that when more data become available, the comet data could be fitted by co-adding a sufficient number of particle spectra of the pyroxene type. The central position and overall width of the pyroxene band could accommodate the comet feature. The positions and strengths of the finer-scale features of individual pyroxene class IDPs vary from particle to particle, and it is possible that the fine structure might tend to cancel out if enough particles were measured. There is no reason, however, to expect that the co-addition of only pyroxene-type spectra would provide the skewness toward shorter wavelengths seen in the comet data.

With the present data set, the best agreement between comet and dust particle spectra is found by co-adding spectra of the pyroxene and layer-lattice silicate type in roughly equal amounts. The fit of this composite spectrum with the data from comet Kohoutek is shown in Figure 9. The silicate bands for particles in the olivine class fall at significantly longer wavelengths than the emission features seen in the comet data, and these particles must have a low abundance in this comet, if they are present at all. Thus, it is possible to match the spectral properties of IDPs with those of the dust of comet Kohoutek, but only at the expense of including the different pyroxene and

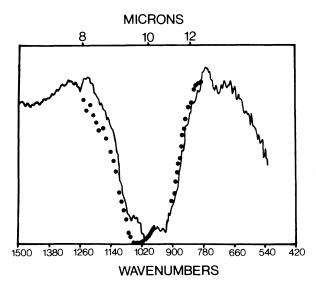


Fig. 9.—A fit to inverted comet Kohoutek emission data obtained by coadding approximately equal amounts of layer-lattice silicate and pyroxene IDP spectra. The solid points are the cometary data.

layer-lattice types of particles and excluding a significant contribution from olivine-type particles.

Because comets are cold and have been stored far out in the solar system, the belief has arisen that they are likely to contain 'primordial material" that escaped processing at the time of the formation of the solar system. A general discussion of this subject can be found in a National Academy of Sciences report written in 1980 entitled "Strategy for the Exploration of Primi-Solar-System Bodies—Asteroids, Comets, Meteoroids." The IDPs may then be representative of the material present when the solar system was in its protostellar phase. Interstellar infrared objects of the Becklin-Neugebauer (BN) type are widely regarded as "protostars" embedded in cool gas-dust clouds from which they are forming (Becklin and Neugebauer 1968; Willner et al. 1982), and it is interesting to compare the spectra of IDPs with the dust signatures in the spectra of these objects. Because of the "primitive" chondritic pattern of elements in the IDPs, such a comparison is warranted independent of a possible cometary link.

In Figure 10 we show a comparison of the spectrum of a layer-lattice silicate IDP with the spectrum of the BN object W33 A (Soifer et al. 1979). Better data are available for W33 A than for comets, permitting a comparison over a much wider range of wavelengths. As can be seen in the figure, W33 A has prominent absorption features at 3.1 μ m, 4.6 μ m, 6.0 μ m, 6.8 μ m, and 9.7 μ m. The 3.1 μ m and 6.0 μ m bands are usually attributed to water ice, and the 9.7 μ m feature to silicates. The 3.1 μ m band is variable in width and probably represents the overlap of several absorbing species present in variable concentrations (Hagen, Allamandola, and Greenberg 1980). Several authors (Puetter et al. 1979; Hagen, Allamandola, and Greenberg 1980; Soifer et al. 1979) have attributed the 6.8 μ m feature to hydrocarbons. This interpretation has been criticized (Willner et al 1982) on the grounds that hydrocarbons should have additional spectral features in the 3.3–3.5 μ m region that are not clearly observed.

As can be seen from Figure 10, the layer-lattice silicate IDP also has bands near 3.0 μ m, 6.0 μ m, 6.8 μ m, and 9.8 μ m. This general correspondence with the W33 A spectrum is intriguing and raises the possibility that the IDPs may consist of

materials similar to those found in interstellar molecular-gas and dust clouds. A major difference would be the presence of ice in the latter but not in the former. This would explain the fact that the 3 μ m feature, which is relatively weak in the IDPs, is a dominant feature of the protostellar spectra. Of course, bands seen in the protostellar spectra that are due to ices will not be represented in the IDP data.

In the previous section we showed that the 6.8 μ m feature in at least one (and likely all) layer-lattice silicate IDP is probably caused by carbonates. We suggest the possibility that a component of the 6.8 μ m feature seen in the spectra of protostars has a similar origin. The 4.6 μ m feature in W33 A has been attributed to CO on grain surfaces (Soifer et al. 1979). Possibly chemical reactions on such grain surfaces could produce carbonates in the form of grain coatings.

The identification of an 11.4 μ m band in protostellar spectra would support the suggestion that carbonates contribute to the absorption at 6.8 μ m. In addition, observation of the 11.4 μ m band would raise the interesting possibility that *some* of the carbonates seen in meteorites may be primary components and not the result of secondary hydrothermal alterations as is currently believed (Macdougall, Lugmair, and Kerridge 1984).

e) Future Work Needed to Clarify the Relationship between IDPs and Astronomical Objects

Throughout this paper we have made the implicit assumption that the properties of the IDPs measured in the laboratory are those that the particles possessed in space prior to atmo-

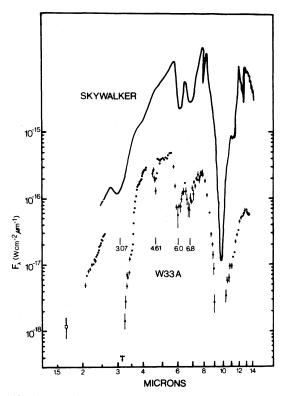


FIG. 10.—A comparison of a layer-lattice silicate IDP spectrum (Skywalker) with a spectrum of the protostellar object W33 A (dots). The relative depth of features should not be compared between the spectra since the protostellar spectrum is plotted against a logarithmic scale, while the IDP spectrum is plotted on an arbitrary linear scale. However, the positions of the bands can be directly compared.

spheric entry. However, all the particles are heated as they slow down from cosmic velocities (Fraundorf 1980). In some cases (e.g., those particles that retain fossil nuclear particle tracks and abundant water) the heating must have been modest (<450°C), while in other cases it must have been severe. It is conceivable that particles in one spectral class could be converted to another class by severe heating (although we consider this to be unlikely based on the TEM observations). Laboratory heating experiments on IDPs that address this issue are currently in progress.

An additional complication may be introduced by IDP sampling biases. The atmospheric impact collectors used to obtain the IDPs do not efficiently collect particles smaller than several microns. If these small particles differ significantly in composition from the larger particles, our collections may not be representative of the bulk of interplanetary dust. There is also evidence that some incoming dust is extremely fragile (Verniani 1973) and may not survive atmospheric entry. Such particles are certainly underrepresented in our collections. Experiments like that presently being flown on the LDEF I orbital platform should help determine if sampling biases are a severe problem (Zinner, Pailer, and Kuczera 1983).

Finally, the particles examined in this study were taken from a small number of collectors. It is possible that Earth intercepts different populations of dust at different times of the year. Clearly, infrared measurements on a much larger set of IDPs from more collectors are necessary. Combined infrared, ion probe, and TEM studies on particles also need to be pursued.

To fit the existing IDP infrared spectra to the spectroscopic properties of comet dust we have found it necessary to combine the spectra of two different types of particles. The layer-lattice silicate class contains water and is a low-temperature assemblage. The pyroxene class is anhydrous. Lathlike pyroxene "whiskers" seen in some IDPs have been interpreted as products of direct solid growth from a gas (Bradley, Brownlee, and Veblen 1983). Thus a comet would have to contain large amounts of disparate substances (though it should be noted that both classes of IDPs have large D/H enrichments indicative of a primitive origin). Such a mixture could be explained if the layer-lattice silicates were simply hydrothermal alteration products of the pyroxene particles. Since abundant H₂O is presumably available in comets, this possibility seems tenable. Such an explanation, however, implies that the pyroxene particles are, in some sense, more primitive than the layer-lattice silicates. Since the D/H enrichments in the IDPs are probably carried by hydrocarbons and not H₂O, the hydrous alteration must have taken place in the presence of isotopically "normal" water.

Almost all the layer-lattice silicate IDPs contain a 6.8 μ m feature, although the strength of this band relative to the silicate feature is highly variable. A critical test of the presence of layer-lattice silicate IDPs in comet dust would be a search for the 6.8 μ m feature in comet dust tails. Because of the opacity of Earth's atmosphere in this spectral region, such a search would have to be performed from the Kuiper Airborne Observatory or (later) from a space-based infrared telescope. We estimate that measurements taken with a spectral resolution $\lambda/\Delta\lambda \geq 50$ and a signal-to-noise ratio sufficient to detect a band $\sim 10\%$ that of the main silicate absorption would suffice for the detection of the 6.8 μ m feature if it is present in the amount required by our composite particle fit to the comet data.

The possibility of a relationship between the 6.8 μ m feature in comets (if it is found) and that in the IDPs would be more certain if the band near 11.4 μ m were also observed in comets.

This band should be about half as strong as the 6.8 μ m band, and considerably narrower. We estimate that a spectral resolution of $\lambda/\Delta\lambda > 200$ and good signal-to-noise ratios will be necessary to clearly observe this band.

We have also noted the possibility that co-addition of a larger number of pyroxene-type spectra might lead to a fit to the cometary data, without the necessity of including layer-lattice silicate particles. The variability in the position and depths of the fine-scale features in the 10 μ m band might act to cancel out most of the distinctive pyroxene features. However, some residual fine structure might remain, and it is desirable to obtain the best possible measurements of the cometary 10 μ m feature in the hopes that diagnostic features might be seen.

Clearly, comet Halley is a candidate for searches for the 6.8 and 11.4 μ m bands and detailed features in the 10 μ m band. There is no reason, at present, to believe that all comets have identical dust components, and detailed spectra of many comets would be valuable for intercometary comparisons as well as for comparisons with IDP spectra.

We also feel that a common origin for the 6.8 μ m features seen in IDPs and protostellar objects should be considered. As with the comets, a critical test of this possibility would be afforded by the observation of an accompanying 11.4 μ m feature. Although there is a suggestion of such a band in some of the protostellar data, better sensitivity and spectral resolution are required to clarify this question.

f) Comments on the Nature and Origin of IDPs

Every technique used to study IDPs demonstrates that they differ considerably one from the other. The very existence of various infrared classes illustrates this fact. Moreover, as we have previously discussed, particles with nearly identical infrared spectra can show distinct differences when examined in detail by transmission electron microscopy. This diversity reflects different formation histories, and it is unlikely that any single, simple picture of IDP formation can be given.

It seems probable, however, that many of the properties of the particles reflect processes that occurred during an early epoch of the solar system, possibly in the molecular gas and dust cloud phase that preceded the formation of the solar nebula.

Following the reasoning developed by Yang and Epstein (1983) in their discussion of deuterium measurements of primitive meteorites, we believe that the large D/H excesses measured in many of the particles provide the strongest evidence for this view. Radio observations of interstellar clouds show that simple molecules such as HCN are greatly enriched in D relative to cosmic D/H abundances (Penzias 1980). The enrichment can be understood in terms of ion-molecule reactions which permit the formation of the thermodynamically more stable heavier molecules at the low temperatures characteristic of dense interstellar clouds (Watson, Anicich, and Huntress 1976; Geiss and Reeves 1981). Complex molecules formed from such D-rich precursors either by photolytic reactions (Greenberg 1982) or by plasma processes (Miller and Urey 1959) would be expected to retain at least a fraction of the original isotopic signatures.

The establishment of isotopic enrichments requires low temperatures. This suggests that the isotopic effects seen in the particles were established during the cold molecular cloud phase prior to solar system formation, or, if the particles were formed during the time of the nebular-protostar phase, they must have been produced in cold regions of space far removed from the warmer regions of the nebula.

The similarity between absorption features measured in the infrared spectra of IDPs and those seen in the spectra of protostars provide a further potential link between interplanetary dust and interstellar molecular cloud material. However, since we have shown that materials with similar infrared properties can have quite different microstructures, this cannot be taken as proof that we are dealing with similar materials. The spectral similarity is nonetheless suggestive.

The presence of (relatively) unaltered prenebular, molecular cloud material in interplanetary dust particles is not unexpected. Some, and perhaps most, of the interplanetary dust cloud must be derived from comets (Whipple 1982), which may contain original nebular material that was not severely processed at the time the Sun and planets were formed.

It is likely that solid material in interstellar clouds, and thus possibly in IDPs, consists of two fundamentally distinct types: those solids that formed in the cloud itself as a result of gasgrain interactions and those solids that were formed near other distant astrophysical sites *prior* to the formation of the cloud. This is a point of view that has been treated in a number of recent papers (see, for example, Clayton 1982). Although there is no direct evidence for the second type of material in IDPs, related isotopic measurements in meteorites strongly suggest that it is likely to be present.

Bulk samples of a few unequilibrated meteorites, as well as the acid residues of many more meteorites, exhibit D/H excesses similar to those seen in IDPs (Kolodny, Kerridge, and Kaplan 1980; Yang and Epstein 1983; Hinton et al. 1983; Zinner, McKeegan, and Walker 1983). It is likely that these isotopic signatures arise in an analogous fashion to those seen in IDPs and show the presence of molecular cloud materials. Meteorites also show other isotopic effects that appear to be due to nucleosynthetic events. The most striking example is Ne-E (Black and Pepin 1969), a noble gas component that consists almost entirely of ²²Ne (Eberhardt 1974). It is probable that Ne-E was produced from radioactive ²²Na which was incorporated into solid material and subsequently decayed to produce pure ²²Ne. Since the half-life of ²²Na is short (2.6 yr), the solid material must have formed close in time (and, hence, in space) to a nucleosynthetic event. Recent observations of other isotopic anomalies correlated with Ne-E have been interpreted as manifestations of interstellar matter in meteorites (Swart et al. 1983).

Unfortunately, nucleosynthetically distinct material represents only a tiny fraction of the mass of even the most primitive meteorites so far studied. Even if it were present in IDPs, the amount may be so small as to preclude its identification.

If, as we think is likely, the material in many IDPs was formed during an early stage of the evolution of the solar system, the diversity of the particles indicates they are sampling a wide variety of processes. Although IDPs may give us a window on the early solar system, the view is certainly not a simple one, and much more work will be required before a full picture can emerge.

V. SUMMARY

Almost all of the 26 "chondritic" stratospheric dust particles studied in the 2.5–25 μ m spectral region have a dominant spectral feature at ~10 μ m. The position and shape of this band vary from particle to particle, but three broad groupings are evident. These spectral groups are labeled olivines, layer-lattice silicates, and pyroxenes by analogy with the infrared spectra of terrestrial mineral standards. Various other bands are also

present in the IDP spectra, including a prominent band at $6.8 \mu m$ that is seen in most of the spectra in the layer-lattice silicate group.

Four of the 26 particles cannot be classified into one of these three infrared classes, although two of them have spectra that are similar to the olivines and pyroxenes. One particle appears to have the spectral characteristics of anhydrous oxides, while the last seems to contain no major phases that are infrared active.

The pyroxene group particles tend to the "fluffy" or "porous," while particles in the other spectral groups tend to be described as "smooth" or "compact." However, more data are needed to see if these trends can be confirmed.

Transmission electron microscopy and laser Raman spectroscopy confirm the infrared classification system. Where they have been measured, for example, particles in the olivine and layer-lattice silicate infrared classes are found to be dominated by the appropriate minerals when viewed by the TEM. The infrared measurements thus give a relatively quick and nondestructive method for identifying the dominant silicate phases in IDPs. However, the TEM results also show that samples with nearly identical infrared spectra can have quite different mineralogical structures when viewed at high magnification. Thus the infrared spectra do not provide a complete characterization of IDPs.

Measurements of D/H ratios and fossil solar flare tracks show that some of the particles in *all* of the major silicate spectral classes are extraterrestrial. It is not certain that *all* chondritic stratospheric dust particles are extraterrestrial, but it seems likely.

The emission spectra of dust from comet Kohoutek cannot be matched with the transmission spectra of any single IDP spectral class. However, a reasonable fit can be obtained by co-adding spectra from approximately equal numbers of particles from the pyroxene and layer-lattice silicate groups. Because of the mismatch in the position and width of the olivine spectra, not many particles in this group can be present in comet Kohoutek.

A search for the 6.8 and 11.4 μ m features in future comet observations would provide a critical test of the spectral matching of IDPs to the comet data. In one particle (Calrissian) the depth of the 6.8 μ m band is comparable to the major 10 μ m silicate feature. The observation of an accompanying narrower and weaker band at 11.4 μ m in this particle suggests that these features are due to carbonate minerals. However, additional work must be done to confirm this interpretation and to determine the chemical and physical state of the carbonates.

Mid-infrared spectra of protostars show strong similarities to the spectra of particles in the layer-lattice silicate group, including a common 6.8 μm band. The possibility exists that this band and the similar one observed in IDPs have common origins. A critical test is a careful astronomical search for the accompanying 11.4 μm band seen in the IDPs.

The large D/H enrichments measured in the carbonaceous components of the IDPs finds a natural explanation if at least some of the material in them was synthesized during an interstellar cloud phase of the evolution of the solar system. Some interstellar clouds are known to have large D/H enrichments in simple molecules such as HCN, and more complex molecules formed from such precursor molecules would be expected to retain some of the original isotopic signature. The infrared data provide a further, albeit weaker, link between the IDPs and interstellar molecular clouds.

By analogy with certain primitive meteorites which show a variety of isotopic effects, we consider it likely that IDPs consist, in part, of two types of interstellar material: that which formed during the interstellar cloud phase and that which formed prior to cloud formation, close in time and place to specific nucleosynthetic events.

Although we consider it likely that IDPs were formed early in the history of the solar system, perhaps predating the formation of the Sun and planets, the heterogeneous character of the particles evidently reflects a complex variety of processes that will take considerable effort to decipher.

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REFERENCES

```
Becklin, E. E., and Neugebauer, G. 1968, Ap. J., 147, 799.
                                                                                                                                                                                                                                             Krätschmer, W., and Huffman, D. R. 1979, Ap. Space Sci., 61, 195.
Liese, H. C. 1975, in Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals, ed. C. Korr, Jr. (New York: Academic), p. 197.
Macdougall, J. D., Lugmair, G. W., and Kerridge, J. F. 1984, Nature, 307, 249.
McKeegan, K. D., Sandford, S. A., Walker, R. M., Wopenka, B., and Zinner, E. 1984, (abstract) Meteoritical Soc. Conf. (Albuquerque, N.M.), 47, S-4.
McKeegan, K. D., Walker, R. M., and Zinner, E. 1985, Geochim. Cosmochim.
      Begemann, F. 1980, Rept. Progr. Phys., 43, 1309.
Black, D. C., and Pepin, R. O. 1969, Earth Planet. Sci. Letters, 6, 395.
Bradley, J. P., and Brownlee, D. E. 1984, (abstract) Meteoritical Soc. Conf. (Albuquerque, N.M.), 47, U-1.
     (Albuquerque, N.M.), 47, U-1.
Bradley, J. P., Brownlee, D. E., and Veblen, D. R. 1983, Nature, 301, 473.
Brownlee, D. E. 1978, in Cosmic Dust, ed. J. A. M. McDonnell (New York: John Wiley), p. 295.
Brownlee, D. E., Ferry, G. V., and Tomandl, D. A. 1976, Science, 191, 1270.
Brownlee, D. E., Pilachowski, L., Olszewski, E., and Hodge, P. W. 1980, in Solid Particles in the Solar System, ed. I. Halliday and B. A. McIntosh
                                                                                                                                                                                                                                                     Acta, submitted.
                                                                                                                                                                                                                                             Acta, submitted.

Merrill, K. M. 1974, Icarus, 23, 566.

Merrill, K. M., and Stein, W. A. 1976, Pub. A.S.P., 88, 285.

Miller, S. L., and Urey, H. C. 1959, Science, 130, 245.

Millman, P. M., Cook, A. F., and Hemenway, C. L. 1973, in Evolutionary and Physical Properties of Meteoroids (NASA SP-319), p. 147.

Morrison, D. A., and Zinner, E. 1975, Proc. Lunar Sci. Conf., 6, 3373.

National Academy of Sciences, Space Science Board, Committee on Planetary and Lunar Exploration, A. G. W. Cameron (chairman). 1980, "Strategy for the Exploration of Primitive Solar-System Bodies—Asteroids Comets and
            (Dordrecht: Reidel), p. 333.
     Brownlee, D. E., Tomandl, D. A., and Olszewski, E. 1977, Proc. Lunar Sci.
            Conf., 8, 149.
     Clanton, U. S., et al. 1982, (abstract) Lunar Planet. Sci. Conf. (Houston, Texas),
            13, 109
   Clayton, D. D. 1982, Quart. J.R.A.S., 23, 174.
Dohnanyi, J. S. 1982, in Cosmic Dust, ed. J. A. M. McDonnell (New York: John Wiley), p. 527.
Eberhardt, P. 1974, Earth Planet. Sci. Letters, 24, 182.
Farmer, V. C. 1974a, in The Infrared Spectra of Minerals, ed. V. C. Farmer (London: Mineralogical Society) p. 285
                                                                                                                                                                                                                                                    the Exploration of Primitive Solar-System Bodies-Asteroids, Comets, and
                                                                                                                                                                                                                                                    Meteoroids: 1980-1990."
                                                                                                                                                                                                                                             Penzias, A. A. 1980, Science, 208, 663.
Poupeau, G., Rajan, R. S., Walker, R. M., and Zinner, E. 1977, in COSPAR: Space Research, Vol. 17, ed. M. J. Rycroft and A. C. Strickland (New York:
           (London: Mineralogical Society), p. 285
                                                                                                                                                                                                                                             Pergamon), p. 599.
Puetter, R. C., Russell, R. W., Soifer, B. T., and Willner, S. P. 1979, Ap. J., 228,
          . 1974b, in The Infrared Spectra of Minerals, ed. V. C. Farmer (London: Mineralogical Society), p. 331.
   1974c, in The Infrared Spectra of Minerals, ed. V. C. Farmer (London: Mineralogical Society), p. 183.
Flynn, G. J., Fraundorf, P., Shirck, J., and Walker, R. M. 1978, Proc. Lunar
                                                                                                                                                                                                                                             Rajan, R. S., Brownlee, D. E., Tomandl, D., Hodge, P. W., Farrar IV, H., and
                                                                                                                                                                                                                                            Rajah, K. S., Browniec, D. E., Tomandi, D., Hodge, F. W., I
Britten, R. A. 1977, Nature, 267, 133.
Rose, L. A. 1979, Ap. Space Sci., 65, 47.
Sandford, S. A. 1983, (abstract) Meteoritics 18, 391.
Sandford, S. A. 1984, Icarus, 60, 115.
Sandford, S. A., and Walker, R. M. 1984a, Bull. AAS, 16, 442.
           Planet. Sci. Conf. 9, 1187.
    Fraundorf, P. 1980, Geophys. Res. Letters, 10, 765.
 Fraundorf, P. 1980, Geophys. Res. Letters, 10, 765.

——. 1981, Geochim. Cosmochim. Acta, 45, 915.

Fraundorf, P., Brownlee, D. E., and Walker, R. M. 1982, in Comets, ed. L. L. Wilkening (Tucson: University of Arizona Press), p. 383.

Fraundorf, P., Hintz, C., Lowry, O., McKeegan, K. D., and Sandford, S. A. 1982a, (abstract) Lunar Planet. Sci. Conf. (Houston, Texas), 13, 225.

Fraundorf, P., McKeegan, K. D., Sandford, S. A., Swan, P., and Walker, R. M. 1982b, J. Geophys. Res., 87, A403.
                                                                                                                                                                                                                                           Sandford, S. A., and Walker, R. M. 1984a, Bull. AAS, 16, 442.

——. 1984b, (abstract) Meteoritical Soc. Conf. (Albuquerque, N.M.), 47, S-3.
Soifer, B. T., Puetter, R. C., Russell, R. W., Willner, S. P., Harvey, P. M., and Gillett, F. C. 1979, Ap. J. (Letters), 232, L53.
Swart, P. K., Grady, M. M., Anders, E., Lewis, R. S., and Pillinger, C. T. 1983, Science, 220, 406.
Tarte, P. 1965, Mem. Acad. Roy. Belgique, Classe Sci., Collection 8°, Vol. 35, Pte. 40, b.
 1982b, J. Geophys. Res., 87, A403.
Fraundorf, P., Patel, R. I., and Freeman, J. J. 1981, Icarus, 47, 368.
Fraundorf, P., Patel, R. I., Shirck, J., and Walker, R. M. 1980, Nature, 286, 866.
Fraundorf, P., Patel, R. I., Walker, R. M., Freeman, J. J., and Adar, F. 1982c, (abstract) Lunar Planet. Sci. Conf. (Houston, Texas), 13, 231.
Fraundorf, P., and Shirck, J. 1979, Proc. Lunar Planet. Sci. Conf., 10, 951.
Geiss, J., and Reeves, H. 1981, Astr. Ap., 93, 189.
Greenberg, J. M. 1982, in Comets, ed. L. L. Wilkening (Tucson: University of Arizona Press), p. 131.
                                                                                                                                                                                                                                                   Pts. 4a-b.
                                                                                                                                                                                                                                            Tomieoka, K., and Buseck, P. R. 1984a, (abstract) Lunar Planet. Sci. Conf.
                                                                                                                                                                                                                                                  (Houston, Texas), 15, 858.
                                                                                                                                                                                                                                                                 . 1984b, (abstract) Meteoritical Soc. Conf. (Albuquerque, N.M.), 47, S-1.
                                                                                                                                                                                                                                            Verni ani, F. 1973, J. Geophys. Res., 78, 8429.
Watson, W. D., Anicich, V. G., and Huntress, W. T. 1976, Ap. J. (Letters), 205,
                                                                                                                                                                                                                                                 L16.5.
   Arizona Press), p. 131.
Grossman, L. 1980, Ann. Rev. Earth Planet. Sci., 8, 559
                                                                                                                                                                                                                                            Wethe rill, G. W., and ReVelle, D. O. 1982, in Comets, ed. L. L. Wilkening
Grossman, L. 1980, Ann. Rev. Earth Planet. Sci., 8, 559.
Hagen, W., Allamandola, L. J., and Greenberg, J. M. 1980, Astr. Ap., 86, L3.
Hanner, M. S. 1980, in Solid Particles in the Solar System, ed. I. Halliday and B.
A. McIntosh (Dordrecht: Reidel), p. 223.
Harvey, G. A. 1973, J. Geophys. Res., 73, 3913.
Herrmann, U., Eberhardt, P., Hildalgo, M. A., Kopp, E., and Smith, L. G. 1978, in COSPAR: Space Research, Vol. 18, ed. M. J. Rycroft and A. C. Strickland (New York: Pergamon), p. 249.
Hinton, R. W., Long, J. V. P., Fallick, A. E., and Pillinger, C. T. 1983, (abstract) Lunar Planet. Sci. Conf. (Houston, Texas), 14, 313.
Hudson, B., Flynn, G. J., Fraundorf, P., Hohenberg, C. M., and Shirck, I. 1981.
                                                                                                                                                                                                                                           (Tuc son: University of Arizona Press), p. 297.
Whipp le, F. L. 1982, in Cosmic Dust, ed. J. A. M. McDonnell (New York: John
                                                                                                                                                                                                                                          Willer, W. B. 1974, in The Infrared Spectra of Minerals, ed. V. C. Farmer (London: Mineralogical Society), p. 227.
Willner, S. P. 1977, Ap. J., 214, 706.
Willner, S. P., et al. 1982, Ap. J., 253, 174.
Yang, J., and Epstein, S. 1983, Geochim. Cosmochim. Acta, 47, 2199.
                                                                                                                                                                                                                                                 (Houston, Texas), 15, 961.
 Hudson, B., Flynn, G. J., Fraundorf, P., Hohenberg, C. M., and Shirck, J. 1981,
                                                                                                                                                                                                                                           Zinner, E., McKeegan, K. D., and Walker, R. M. 1983, Nature, 305, 119.
Hughes, G. W. 1978, in Cosmic Dust, ed. J. A. M. McDonnell (New York: John Wiley), p. 123.
Kolodny, Y., Kerridge, J. F., and Kaplan, I. R. 1980, Earth Planet. Sci. Letters, 46, 149.
        Science, 211, 383
                                                                                                                                                                                                                                           Zinner, E., Pailer, N., and Kuczera, H. 1983, Adv. Space Res., 2, 251.
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SCOTT A. SANDFORD and ROBERT M. WALKER: McDonnell Center for the Space Sciences, Washington University Physics Department, Box 1105, St. Louis, MO 63130